200°. For this reason one may expect the function sum in this case to give a considerably lower entropy value than that obtained by the more accurate graphical method.

The following combinations were found to fit the experimental data on chromic oxide and chromous chloride to above 100°.

$$C_{Cr_2O_3} = D\left(\frac{362}{T}\right) + 2E\left(\frac{470}{T}\right) + 2E\left(\frac{780}{T}\right)$$

$$C_{CrCl_2} = D\left(\frac{82}{T}\right) + E\left(\frac{226}{T}\right) + E\left(\frac{444}{T}\right)$$

TABLE VI

ENTROPY DATA

	Cr	Cr_2O_3	$CrCl_3$
Extrap. (0–56.2), °K.	0.22	0.53	3.96
Graph (56.2–298.1), °K.	5.46	18.84	24.24
$S°_{298.1}$ graphical	5.68 ± 0.05	19.4 ± 0.2	28.2 ± 1.0
$S°_{298.1}$ calcd. from functions		18.0	
		$CrCl_2$	
Extrap. (0–44.7), °K.		5.05	
Graph (44.7–298.1), °K.		22.36	
$S°_{298.1}$ graphical		27.4 ± 0.7	
$S°_{298.1}$ calcd. from functions		27.6	

Table VI gives the results of the entropy calculations.

Related Thermal Data

Thermal data relating to these materials and the source are given in Table VII.

TABLE VII

THERMAL DATA

	$\Delta H_{298.1}$	$\Delta F°_{298.1}$	$S_{298.1}$ This report	$S_{298.1}$
Cr			5.68	
Cr_2O_3	−288,900[a]	−269,400[c]	19.4	
$CrCl_2$	− 92,750[b]	− 84,008[b]	27.4	29.7[b]
$CrCl_3$	−129,565[b]	−113,253	28.2	31.0[b], 31.2[d]

[a] Roth and Becker, *Z. physik. Chem.*, **A145**, 467 (1930).

[b] Doerner, U. S. Bureau of Mines (in press).

[c] Calculated from $\Delta H_{298.1}$ and entropies.

[d] Trapeznikowa, Schubnikow and Miljutin, *Physik. Z. Sowjetunion*, 9, 237 (1936).

Summary

The heat capacities of chromium, chromic oxide and chromous and chromic chlorides at low temperatures have been determined and their corresponding entropies calculated as 5.68, 19.4, 27.4 and 28.2, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary Systems $KClO_3$–K_2SO_4–H_2O and $NaClO_3$–Na_2SO_4–H_2O[1]

BY JOHN E. RICCI AND NICHOLAS S. YANICK

Introduction

This study is part of a systematic investigation of ternary systems involving sodium and potassium chlorates, a series of systems of which several examples are already to be found in the literature. No double salts containing sodium chlorate have yet been reported, the only ternary systems studied being $NaClO_3$–Na_2CO_3–H_2O, $NaClO_3$–$NaCl$–H_2O and $NaClO_3$–$KClO_3$–H_2O.[2] Similarly, in the systems involving potassium chlorate that have been investigated, no compounds are found (-H_2O + KCl, K_2CO_3, $NaClO_3$[2]; also +KBr and KI[3]); potassium chlorate however is found to form solid solutions in the systems $KClO_3$–KNO_3–H_2O and $KClO_3$–$TlClO_3$–H_2O.[2]

As for the sulfates in the present systems, while sodium sulfate is known to form both various double compounds and solid solutions with other sodium salts, potassium sulfate, in systems so far studied, forms no double salts with other potassium salts, but does form solid solutions with potassium chromate and potassium molybdate.[2]

In the present investigation potassium chlorate and potassium sulfate show no complex formation, while the sodium salt system forms one double salt, $NaClO_3 \cdot 3Na_2SO_4$. As for the other sodium halogenates, sodium sulfate forms similar compounds with sodium iodate, namely, $NaIO_3 \cdot 3Na_2SO_4$ and $NaIO_3 \cdot 4Na_2SO_4$,[4] while with sodium bromate it forms no definite compound but a solid solution.[5]

Experimental Methods

The experimental procedure was that usually described for similar investigations. Weighed complexes of known composition were brought to equilibrium by stirring in a

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[1] Presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

[2] "International Critical Tables," Vol. IV, 1928.

[3] Author's unpublished data.

[4] Foote and Vance, *Am. J. Sci.*, **19**, 203 (1930).

[5] Ricci, THIS JOURNAL, **57**, 805 (1935).

large water-bath in which the temperature was maintained constant to ±0.02°. The time required for attainment of equilibrium was determined by analysis, and varied from a few days in the case of the potassium salts, to several weeks in some cases of the sodium salt system. The order of mixing of the components, and the process of "seeding" or inoculation for required phases, had to be varied in accordance with the phase sought. All the solid phases involving sodium sulfate show a considerable tendency to persist in metastable equilibrium, and these metastable phases sometimes change only very slowly to the stable form even with repeated seeding. The densities reported for some of the isotherms were obtained by means of volumetric pipets calibrated for delivery.

The method of analysis of the saturated solution was the same in both systems. In one sample of the solution the chlorate was determined by a volumetric method; in another sample the total solid was determined by evaporation to dryness at 100° followed by 250°; and the sulfate was then calculated by difference. For the chlorate determination, the method of Peters and Deutschländer[6] was used: to the chlorate sample (containing about 0.11 g. of ClO_3^-) is added a definite volume (50 cc.) of 0.05 *M* arsenious oxide solution (previously standardized against pure sodium chlorate by the same procedure); after the addition of a trace of potassium bromide, the solution is acidified strongly with hydrochloric acid and boiled for ten minutes. The excess arsenious oxide is then titrated by Győry's method,[7] by means of 0.033 *M* potassium bromate solution (previously compared with the arsenite solution) using indigo sulfonic acid as indicator.

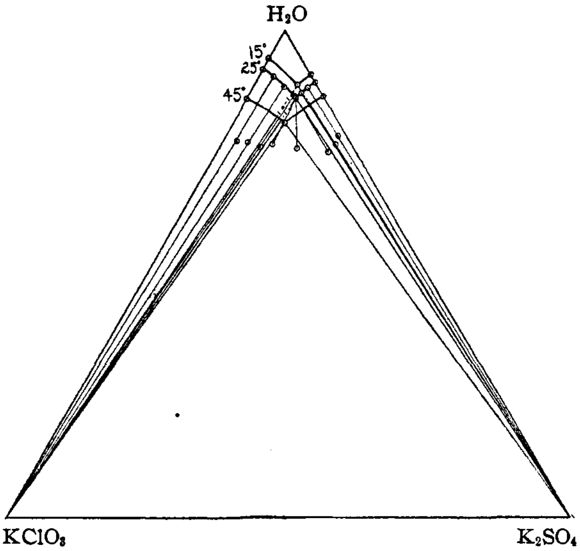

Fig. 1.—System $KClO_3$–K_2SO_4–H_2O.

For the identification of known solid phases, microscopic examination and algebraic extrapolation of tie-lines sufficed. The determination of the formula of the new double salt however was more difficult. Direct analysis of the crystals was not successful; the salt is always incongruently soluble; the crystals were very small, always contaminated with a mother liquor highly concentrated with respect to sodium chlorate, and readily decomposed by washing; even centrifuged residues contained large amounts of mother liquor or of its crystallized salts. Dehydration of residues over various drying agents showed no break in the drying–time curve, so that the solid appeared to be anhydrous. This however is also very clearly seen from the definite convergence of all the tie-lines for complexes giving the double salt as single solid phase, on a point on the $NaClO_3$–Na_2SO_4 side of the triangle. Considering the wide spread of the solubility curve of the double compound at the various temperatures employed, and the fact that the compound is anhydrous, these extrapolations constitute a sufficiently accurate determination of the formula of the double salt. Extrapolating 38 such tie-lines, covering the three different temperatures at which the double salt was obtained, to the point on the base of the triangle representing the formula $NaClO_3 \cdot 3Na_2SO_4$ (containing 80.01% Na_2SO_4), the average absolute error of the extrapolations was 0.63% and the average algebraic error only +0.06%, in sodium sulfate. A further check on the formula was made by means of a method due to Bijlert;[8] two different complexes, of definite compositions, calculated to give the double salt (in metastable equilibrium) were made up, with the addition of a definite amount of a fourth component, sodium chloride, to each. By means of a complete analysis, when equilibrium had been reached, both of the saturated solution and of a wet residue, the amount of mother liquor contained in the wet residue was calculated through the sodium chloride content, thus making possible quite an accurate determination of the composition of the double salt. The results again gave an anhydrous compound, with 80.45 and 80.24% Na_2SO_4 in the two different runs, as compared with 80.01% calculated from the formula $NaClO_3 \cdot 3Na_2SO_4$.

Results

System $KClO_3$–K_2SO_4–H_2O.—The results on this system are given in Table I, and the curves for the three temperatures are shown in condensed form in Fig. 1. No complex formation is observed, the only solid phases being potassium chlorate and potassium sulfate.

System $NaClO_3$–Na_2SO_4–H_2O.—The experimental data for the four temperatures studied (75, 45, 25 and 15°) are presented in Tables II–V, the isotherms being shown graphically in Figs. 2–5. (In these tables, the abbreviation "D.S." stands for "double salt," while (m) indicates metastable phases.)

75° Isotherm.—The solid phases at this temperature are Na_2SO_4 for the curve a-b, $NaClO_3 \cdot 3Na_2SO_4$ for b-c, and $NaClO_3$ for c-d. As may be seen from the diagram, the double salt exists as a stable phase over a short range of variation of

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[6] Peters and Deutschländer, *Apoth. Z.*, 594 (1926); see Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, New York, N. Y., 1929, p. 465.

[7] Győry, *Z. anal. Chem.*, **32**, 415 (1893).

[8] Bijlert, *Z. physik. Chem.*, **8**, 343 (1891); see also Bancroft, *J. Phys. Chem.*, **6**, 178 (1902).

TABLE I

$KClO_3$–K_2SO_4–H_2O

Original complex, wt. %		Satd. soln., wt. %			
$KClO_3$	K_2SO_4	$KClO_3$	K_2SO_4	Density	Solid phase
		45°			
0.00	...	0.00	13.53		K_2SO_4
12.23	19.51	9.80	9.13		$K_2SO_4 + KClO_3$
21.04	7.99	9.80	9.12		$K_2SO_4 + KClO_3$
Av. (of 2)		9.80	9.13		$K_2SO_4 + KClO_3$
...	0.00	13.90	...		$KClO_3$
		25°			
0.00	...	0.00	10.76	1.083	K_2SO_4
1.60	20.02	1.80	9.93	1.089	K_2SO_4
2.89	20.42	3.30	9.43	1.099	K_2SO_4
4.95	19.80	4.95	8.66	1.102	$K_2SO_4 + KClO_3$
10.03	14.01	4.96	8.62	1.100	$K_2SO_4 + KClO_3$
16.03	9.11	4.96	8.62	1.099	$K_2SO_4 + KClO_3$
Av. (of 3)		4.96	8.64	1.100	$K_2SO_4 + KClO_3$
16.51	7.20	5.06	8.19	1.099	$KClO_3$
18.04	4.85	5.77	5.57	1.080	$KClO_3$
20.06	2.35	6.72	2.73	1.063	$KClO_3$
...	0.00	7.897	0.00	1.048	$KClO_3$
		15°			
0.00	...	0.00	9.258	1.076	K_2SO_4
3.51	20.02	3.29	7.86	1.085	$K_2SO_4 + KClO_3$
18.01	7.01	3.29	7.86	1.084	$K_2SO_4 + KClO_3$
Av. (of 2)		3.29	7.86	1.085	$K_2SO_4 + KClO_3$
...	0.00	5.676	0.00	1.032	$KClO_3$

TABLE II

$NaClO_3$–Na_2SO_4–H_2O AT 75°

Original complex, wt. %		Satd. soln., wt. %		
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4	Solid phase
0.00	...	0.00	30.33	Na_2SO_4
5.00	39.96	6.26	24.70	Na_2SO_4
23.98	21.10	27.19	10.56	Na_2SO_4
33.07	11.98	35.05	6.88	Na_2SO_4
42.22	10.06	45.51	3.19	Na_2SO_4
46.11	10.03	50.00	2.39	Na_2SO_4
44.98	14.99	51.85	2.09	Na_2SO_4
50.91	6.88	53.63	1.92	Na_2SO_4
51.71	7.02	54.59	1.73	Na_2SO_4
52.11	8.06	55.78	1.57	Na_2SO_4 + D.S.
52.98	6.89	55.62	1.51	Na_2SO_4 + D.S.
53.08	7.04	55.74	1.49	Na_2SO_4 + D.S.
Av. (of 3)		55.71	1.52	Na_2SO_4 + D.S
55.14	6.09	57.81	1.61	Na_2SO_4 (m)
39.76	10.88	41.42	5.11	D.S. (m)
40.68	12.01	42.98	4.50	D.S (m)
44.98	8.44	46.82	3.27	D.S. (m)
47.80	7.92	49.91	2.51	D.S. (m)
48.88	7.97	51.15	2.28	D.S. (m)
50.73	6.95	52.84	1.94	D.S. (m)
51.09	6.98	53.20	1.99	D.S. (m)
53.49	5.02	54.90	1.84	D.S. (m)
54.17	6.11	56.25	1.62	D.S.
54.99	6.02	57.26	1.30	D.S.
56.63	5.00	58.34	1.37	D.S.
56.83	6.89	59.79	1.05	D.S.
58.13	5.00	60.10	1.14	D.S.
59.30	6.89	60.56	1.05	D.S. + $NaClO_3$
62.19	3.01	60.80	0.93	D.S. + $NaClO_3$
Av. (of 4)		60.73	1.00	D.S. + $NaClO_3$
...	0.00	61.40	0.00	$NaClO_3$

TABLE III

$NaClO_3$–Na_2SO_4–H_2O AT 45°

Original complex, wt. %		Satd. soln., wt. %		
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4	Solid phase
0.00	...	0.00	32.08	Na_2SO_4
15.09	30.07	17.88	17.52	Na_2SO_4
25.59	25.60	31.36	9.03	Na_2SO_4
33.22	14.33	36.12	6.87	Na_2SO_4
34.62	14.28	37.97	6.09	Na_2SO_4
35.01	20.05	41.84	4.61	Na_2SO_4
41.76	12.20	45.88	3.55	Na_2SO_4
45.12	10.03	48.64	2.80	Na_2SO_4
46.14	10.07	49.76	2.53	Na_2SO_4 + D.S.
44.15	15.05	49.66	2.60	Na_2SO_4 + D.S.
Av. (of 2)		49.71	2.57	Na_2SO_4 + D.S.
49.05	7.01	51.46	2.38	Na_2SO_4 (m)
20.18	21.28	20.10	18.68	D.S. (m)
27.78	15.92	28.23	12.66	D.S. (m)
32.94	13.03	33.73	9.13	D.S. (m)
36.96	10.04	37.67	7.00	D.S. (m)
39.03	10.04	40.14	5.85	D.S. (m)
42.14	9.01	43.56	4.45	D.S. (m)
44.99	6.98	46.18	3.57	D.S. (m)
47.03	8.96	49.48	2.67	D.S. (m)
47.17	10.04	50.22	2.40	D.S.
48.59	10.06	51.79	2.21	D.S.
49.13	10.04	52.57	1.97	D.S.
49.83	9.97	53.16	1.80	D.S. + $NaClO_3$
55.32	6.06	53.02	1.85	D.S. + $NaClO_3$
60.95	2.11	53.12	1.70	D.S. + $NaClO_3$
Av. (of 5)		53.10	1.77	D.S. + $NaClO_3$
...	0.00	54.59	0.00	$NaClO_3$

TABLE IV

$NaClO_3$–Na_2SO_4–H_2O AT 25°

Original complex, wt. %		Satd. soln., wt. %		
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4	Solid phase
0.00	...	0.00	21.78	$Na_2SO_4 \cdot 10H_2O$
5.13	24.11	6.58	18.20	$Na_2SO_4 \cdot 10H_2O$
10.04	21.02	12.30	15.77	$Na_2SO_4 \cdot 10H_2O$
15.09	18.99	18.05	13.90	$Na_2SO_4 \cdot 10H_2O$
20.98	15.99	23.45	12.64	$Na_2SO_4 \cdot 10H_2O$
25.94	13.76	27.36	12.06	$Na_2SO_4 \cdot 10H_2O$
27.50	14.00	28.92	12.21	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
27.37	14.74	28.87	12.03	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
Av. (of 2)		28.90	12.12	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
22.80	19.32	29.29	12.23	$Na_2SO_4 \cdot 10H_2O$ (m)
26.32	15.50	29.52	12.20	$Na_2SO_4 \cdot 10H_2O$ (m)
27.46	15.52	29.90	12.25	$Na_2SO_4 \cdot 10H_2O$ (m) + D.S. (m)
26.30	18.34	29.89	12.27	$Na_2SO_4 \cdot 10H_2O$ (m) + D.S. (m)
Av. (of 2)		29.90	12.26	$Na_2SO_4 \cdot 10H_2O$ (m) + D.S. (m)
0.00	...	0.00	33.97	Na_2SO_4 (m)

TABLE IV (*Concluded*)

Original complex, wt. %		Satd. soln., wt. %		
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4	Solid phase
5.06	40.13	6.03	28.62	Na_2SO_4 (m)
14.92	30.09	17.09	19.89	Na_2SO_4 (m)
26.99	15.96	28.02	12.53	Na_2SO_4 (m)
29.20	18.89	32.47	9.86	Na_2SO_4
34.89	15.02	38.07	7.21	Na_2SO_4
38.04	15.05	42.39	5.37	Na_2SO_4
39.91	15.01	44.76	4.60	Na_2SO_4
44.56	8.07	46.28	4.02	Na_2SO_4 + D.S.
45.84	5.06	46.26	4.02	Na_2SO_4 + D.S.
46.01	5.02	46.40	3.99	Na_2SO_4 + D.S.
Av. (of 3)		46.31	4.01	Na_2SO_4 + D.S.
25.00	19.02	25.26	15.72	D.S. (m)
26.83	16.94	27.00	14.75	D.S. (m)
30.30	15.19	30.80	11.90	D.S. (m)
31.07	15.04	31.65	11.35	D.S. (m)
31.92	15.09	32.71	10.65	D.S. (m)
33.19	13.48	33.85	9.93	D.S. (m)
33.49	14.05	34.36	9.61	D.S. (m)
35.00	13.08	36.08	8.56	D.S. (m)
36.07	13.06	37.31	7.91	D.S. (m)
39.10	9.05	39.75	6.70	D.S. (m)
39.80	11.04	41.19	5.99	D.S. (m)
43.03	8.06	44.10	4.76	D.S. (m)
42.49	11.03	44.55	4.75	D.S. (m)
45.03	14.98	46.57	3.83	D.S. + $NaClO_3$
46.98	5.50	46.63	3.89	D.S. + $NaClO_3$
53.24	4.03	46.68	3.83	D.S. + $NaClO_3$
Av. (of 7)		46.62	3.87	D.S. + $NaClO_3$
48.67	4.55	46.63	3.88	Na_2SO_4 (m) + $NaClO_3$ (m)
48.46	6.20	46.64	3.85	Na_2SO_4 (m) + $NaClO_3$ (m)
Av. (of 2)		46.64	3.86	Na_2SO_4 (m) + $NaClO_3$ (m)
54.99	2.40	47.62	2.80	$NaClO_3$
...	0.00	50.14	0.00	$NaClO_3$

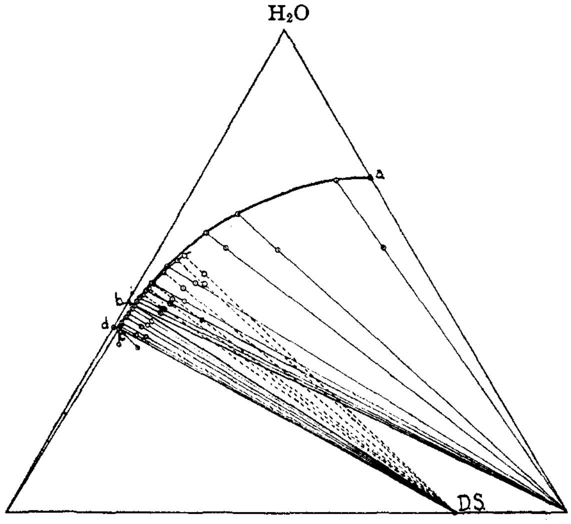

Fig. 2.—75° Isotherm: $NaClO_3$–Na_2SO_4–H_2O.

TABLE V

$NaClO_3$–Na_2SO_4–H_2O AT 15°

Original complex, wt. %		Satd. soln., wt. %			
$NaClO_3$	Na_2SO_4	$NaClO_3$	Na_2SO_4	Density	Solid phase
0.00	...	0.00	11.60	1.106	$Na_2SO_4·10H_2O$
15.02	15.00	19.86	5.52	1.200	$Na_2SO_4·10H_2O$
27.01	13.02	34.75	4.06	1.323	$Na_2SO_4·10H_2O$
31.93	9.54	36.89	4.15	1.348	$Na_2SO_4·10H_2O$
35.00	8.49	39.37	4.02	1.372	$Na_2SO_4·10H_2O$
36.97	8.02	41.16	3.92		$Na_2SO_4·10H_2O$
39.99	6.77	43.07	3.89		$Na_2SO_4·10H_2O$
41.20	6.19	43.67	3.90		$Na_2SO_4·10H_2O$
41.97	13.08	44.14	4.03	1.422	$Na_2SO_4·10H_2O$ + $NaClO_3$
44.96	10.03	44.10	4.09	1.422	$Na_2SO_4·10H_2O$ + $NaClO_3$
Av. (of 2)		44.12	4.06	1.422	$Na_2SO_4·10H_2O$ + $NaClO_3$
34.51	12.52	35.93	8.91	1.393	Na_2SO_4 (m)
36.49	12.51	38.37	7.98	1.408	Na_2SO_4 (m)
41.93	13.00	41.77	6.52		Na_2SO_4 (m) + $NaClO_3$ (m)
44.93	10.00	41.92	6.36	1.424	Na_2SO_4 (m) + $NaClO_3$ (m)
Av. (of 2)		41.85	6.44	1.424	Na_2SO_4 (m) + $NaClO_3$ (m)
52.00	4.55	42.66	5.59		$NaClO_3$ (m)
55.99	3.00	44.34	3.83	1.422	$NaClO_3$
55.94	1.70	45.86	2.19	1.423	$NaClO_3$
...	0.00	47.91	0.00	1.406	$NaClO_3$

only 5% in respect to sodium chlorate, but its solubility curve has been followed as a metastable equilibrium as far as 41% $NaClO_3$ (a total range of 15% on the diagram). The same behavior is observed at the other temperatures (45 and 25°), where the range of stability is even smaller (3.4

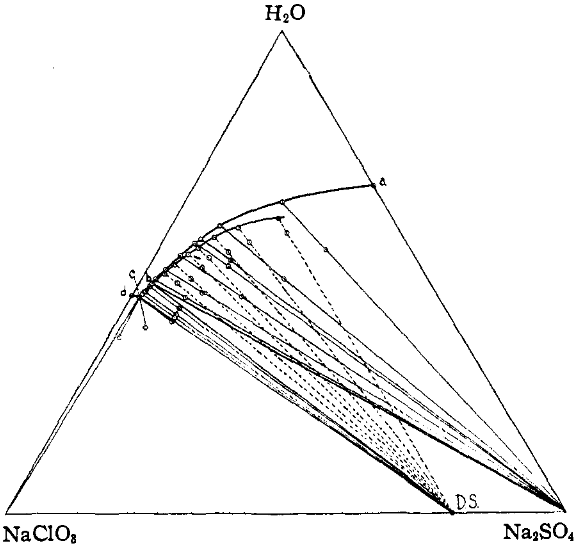

Fig. 3.—45° Isotherm: $NaClO_3$–Na_2SO_4–H_2O.

and 0.3%, respectively); at 45° the total range recorded is 33%, and at 25°, 22%. Possibly these curves could be followed even further, but a point of congruent saturation was not reached in the present work. Another peculiarity of this double compound to be pointed out is the extreme slowness with which the phase, when present in a metastable state (fine, lustrous, needle-shaped crystals) yields, on seeding, to the formation of the stable sodium sulfate. In fact mere seeding never gave a complete change from the metastable to the stable curve. The stable curve for sodium sulfate is obtained only by taking care to prevent seeding with the double salt; otherwise crystals of the latter forming temporarily or accidentally persist in an extraordinary manner.

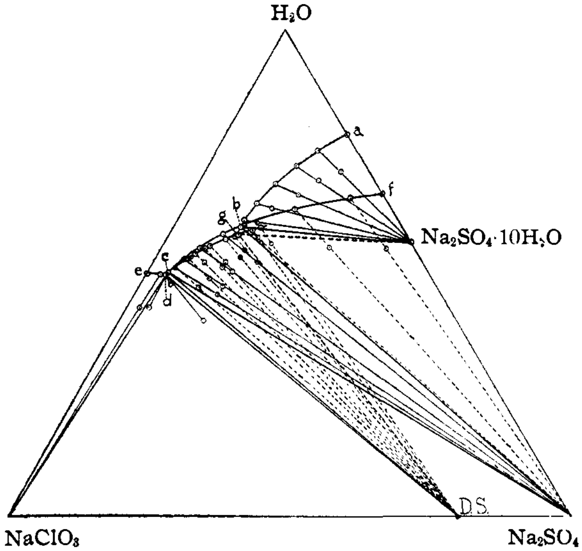

Fig. 4.—25° Isotherm: $NaClO_3$-Na_2SO_4-H_2O.

45° Isotherm.—Phases and general relations just as at 75°.

25° Isotherm.—The stable phases and their solubility curves are as follows: $Na_2SO_4 \cdot 10H_2O$, for a-b; Na_2SO_4 for b-c; $NaClO_3 \cdot 3Na_2SO_4$ for c-d; and $NaClO_3$ for d-e. The curve b-f is the metastable extension of the sodium sulfate solubility curve, point f being the metastable solubility of sodium sulfate at 25°. The double salt curve extends for a considerable distance beside the stable sodium sulfate curve, and meets a metastable extension of a-b at the point g, which is therefore an isothermally invariant solution in metastable equilibrium with $Na_2SO_4 \cdot 10H_2O$ and the double salt.

As already stated the stable range for the double salt at this temperature appears to be extremely short. Because of the close similarity of the slopes of the sodium sulfate and double salt curves, the narrowness of the isothermally invariant area for the ocurrence of both phases together, the slowness with which transformations take place, and the tendency for solutions to remain in metastable equilibrium with either sodium sulfate or double salt separately, the isothermally invariant point for the two solid phases sodium sulfate + double salt is very difficult to obtain at all three temperatures, especially at 25°. At 25° seven complexes gave a solution with the composition 46.62% $NaClO_3$ and 3.87% Na_2SO_4, with sodium chlorate and double salt as solid phases. Two complexes, with sodium chlorate and sodium sulfate apparently as solid phases, gave the same composition, 46.64% $NaClO_3$ and 3.86% Na_2SO_4. The former are probably stable, the latter metastable. Probably the most that can be said with certainty from the data is that the quintuple point representing the disappearance of the double salt as a stable phase (with lowering temperature) must occur at a temperature close to and probably slightly below 25°.

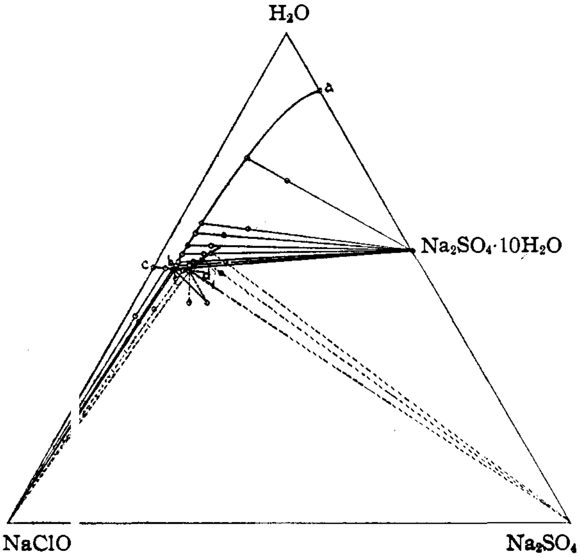

Fig. 5.—15° Isotherm: $NaClO_3$-Na_2SO_4-H_2O.

15° Isotherm.—The only stable solid phases at this temperature are $Na_2SO_4 \cdot 10H_2O$ for the curve a-b, and $NaClO_3$ for b-c. The point d is an isothermally invariant solution in metastable equilibrium with sodium chlorate and anhydrous sodium sulfate; the curve for the solubility of the latter could be followed for only a short distance, being extremely unstable. At this temperature, finally, the double salt is not stable at all; it formed only as a temporary metastable phase a few times, but was too labile in respect to the decahydrate to allow any part of its solubility curve to be determined.

Summary

1. Solubility measurements are given for the system $KClO_3$–K_2SO_4–H_2O at 15, 25 and 45°; no double salt formation is found in this system.

2. The system $NaClO_3$–Na_2SO_4–H_2O has been studied at 15, 25, 45 and 75°. A double salt with the formula $NaClO_3 \cdot 3Na_2SO_4$ is formed at 25° and above, having always a very short range of stable existence, but persisting in metastable equilibrium over a very considerable range of concentration.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Potassium Hydroxide Solutions from Electromotive Force Measurements

BY HERBERT S. HARNED AND MELVIN A. COOK[1]

The electromotive forces of the cell

$$H_2 \mid KOH(m_2) \mid K_xHg \mid KOH(m_1) \mid H_2 \qquad (1)$$

have been measured at 25° by Knobel.[2] Following the procedure which Harned and Hecker[3] employed with sodium hydroxide solutions, a thorough investigation of these cells has been made. Measurements have been obtained from 0 to 35° at 5° intervals and at concentrations from 0.1 to 4 *M*. For purposes of theoretical computations, these measurements have been supplemented with density determinations over the above ranges of temperature and concentration. From these data, the activity coefficient, the relative partial molal heat content and the relative partial molal heat capacity of this hydroxide have been computed.

Experimental Results

The method of measurement and cell technique was with slight modification the same as described by Harned,[4] and Harned and Hecker.[3] The hydrogen electrodes were of the usual platinized platinum foil type. The potassium amalgam was prepared as described by Harned and was approximately 0.02% potassium. The temperature control was ±0.02°. A stock solution of 5 *M* potassium hydroxide was made from the highest grade analyzed chemical. The carbonate present was removed by addition of a slight excess of a barium hydroxide solution. The solution was then boiled under vacuum, and kept under an atmosphere of hydrogen. From this solution a reference solution of 0.05 *M* hydroxide was made. The solutions of varying concentrations were made from the 5 *M* stock solution by weight dilution with water. Potassium hydroxide solutions were analyzed by titration with a gravimetrically standardized hydrochloric acid solution. The concentrations were all known to within ±0.05%.

The densities of the solutions were obtained by means of dilatometers in the manner described by Harned, Keston and Donelson.[5]

The measurements of the electromotive forces were made with a Leeds and Northrup Type K potentiometer. Results were obtained at 25 different potassium hydroxide concentrations and at 5° intervals from 0 to 35°. Duplicate or triplicate results were obtained at each concentration and temperature. The results, all of which were reproducible to within ± 0.08 mv., were smoothed to round concentrations by plotting the function $(E - 2k \log m/0.05)$, where k is $2.303\ RT/F$, against the molality. 8.315, $t + 273.1$ and 96,500 were employed for R, T and F, respectively. Since a table of all these results is voluminous, we have resorted to the expediency of expressing the electromotive forces at a given concentration by means of the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

The constants of this equation were determined by the graphical method used by Harned and Nims.[6] The values of E_{25}, a and b are given in

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[1] This communication contains part of the material of a dissertation to be presented by Melvin A. Cook to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1937.

[2] Knobel, THIS JOURNAL, **45**, 70 (1923).

[3] Harned and Hecker, *ibid.*, **55**, 4838 (1933).

[4] Harned, *ibid.*, **47**, 677 (1925).

[5] Harned, Keston and Donelson, *ibid.*, **58**, 989 (1936).

[6] Harned and Nims, *ibid.*, **54**, 423 (1932).